Reliability of Hg Concentration Measurements in Archived Soil and Peat Samples

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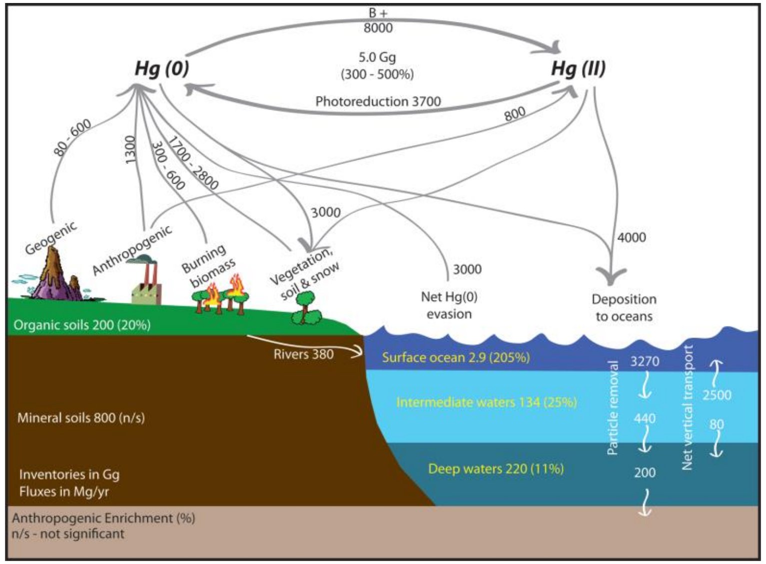
Importance of Soils in the Global Hg Cycle

- Largest global store of Hg – equivalent to >100 yrs of annual emissions
- Soil store mediates changes due to anthropogenic emissions – re-emission
- Need to know the fate of Hg stored in soils – how much is permanently sequestered?
- How are Hg soil pools changing through time?



Driscoll et al., 2013, ES&T, 47: 4967-4983.

Can Soil Samples be Archived for Hg Analysis?

- Help us understand how Hg in soils is responding to changes in global emissions
- Andre DeSaules, Swiss Soil Monitoring Network – possible uneven drying, volatilization, cross-contamination (DeSaules, 2012, Environ. Monit. Assess. 184:487–502)
- Published studies have reported Hg concentrations in archived soils, but no evaluation of effects of storage on Hg concentrations

Opportunistic Study

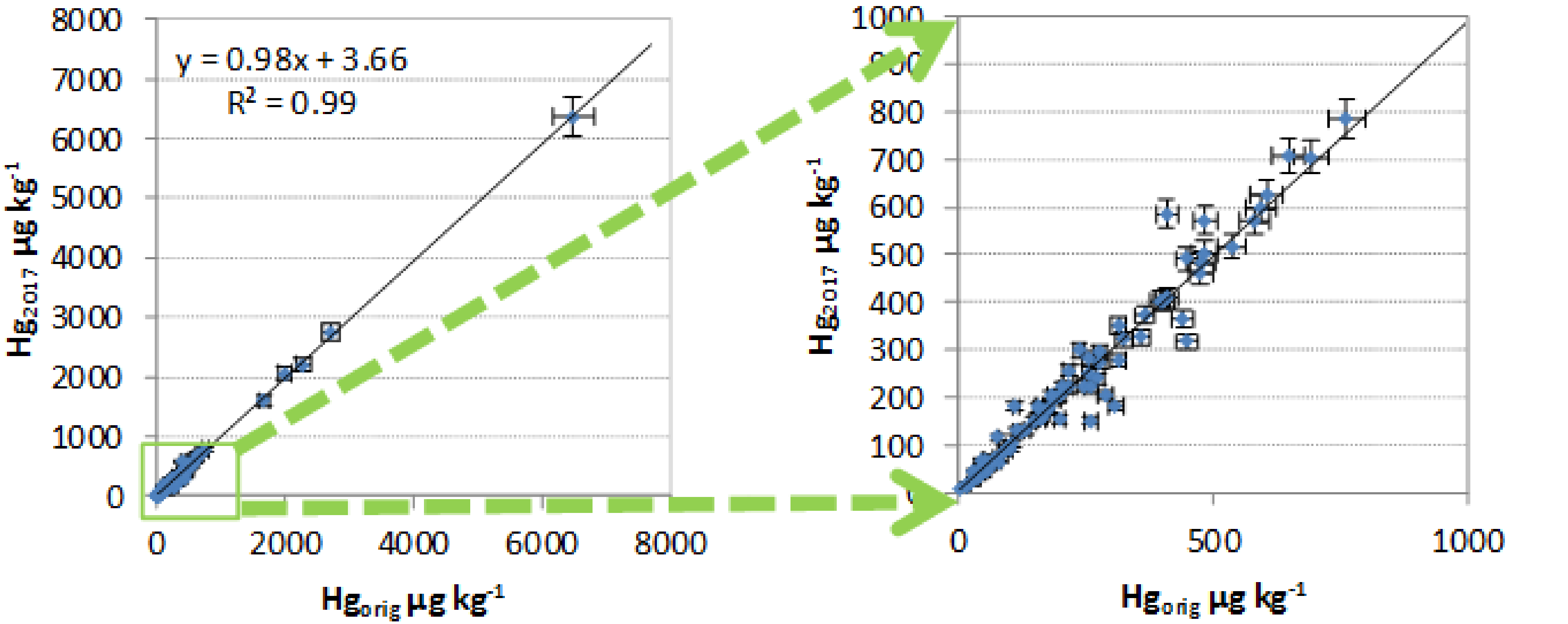
- Re-analyze soil and peat samples from 6 sites in Czech Republic
- Sites varied in their exposure to Hg pollution – one site near smelter
- Sieved – most were air dried, but some were freeze dried
- Samples stored at room temperature, zip-lock polyethylene bags
- Samples shaken, quartered, one quarter selected for analysis
- Total Hg – cold-vapor atomic absorption spectrometry

General Sample Data

Site	PL	PRI	TOK	LES	LYS	NPBS
Location	48.777°N, 13.867°E	49.697°N,* 13.997°E	49.711°N, 13.891°E	49.976°N, 14.776°E	50.034°N, 12.669°E	50.858°N, 14.404°E
Elevation (m a.s.l.)	1089 - 1378	476 - 569	865	406 - 505	829 - 949	281 - 366
Mean annual temp. (°C)	4.7	7.3	5.5	8.4	5.0	8.0
Mean annual precip. (mm)	1188	623	710	613	934	800
Bedrock	granite	greywackes, conglomerates, clastic sediments	conglomerates	granite	granite	sandstone
Soils	Podzol, Dystric Cambisol, Leptosol	Dystric Cambisol	peat	Dystric Cambisol	Albic Podzol	Entic Podzol
Treatment	air dried	air dried	air dried	freeze dried	freeze dried	freeze dried
Storage vessel	PE bottle 500 ml	PE container 50 ml	PE container 25 ml	PE bottle 100 ml	PE plastic bag	PE plastic bag
Storage state	fraction < 2 mm	pulverized	pulverized	pulverized	pulverized	pulverized
Organic soil (TC > 10%)	x	x	x	x	x	x
Mineral soil (TC < 10%)	x	x		x	x	x
Land cover	forest	forest, agr. field	peatland	forest	forest	forest
n	29	16	10	13	6	8
Year of original Hg analysis	2000	2005	2006	2006	2007	2007
Original mean Hg (μg kg^{-1})	205	1219	251	231	330	100
Original range	33-479	73-6485	162-404	20-763	43-649	6-485
2017 mean Hg (μg kg^{-1})	204	1212	253	226	327	107
2017 range	38-585	74-6363	156-404	20-785	37-708	7-572
Mean C (%)	10.9	16.1	32.6	21.2	10.9	6.3
Mean N (%)	0.6	0.1	1.0	0.1	0.5	0.3
Mean S (%)	0.06	0.61	ND	0.20	0.14	0.06
Reference	unpublished data	Ettler et al. 2007	Ettler et al. 2008	Navrátil et al. 2014	Navrátil et al. 2014	Navrátil et al. 2009

* coordinates of Pb smelter, ND - means no data

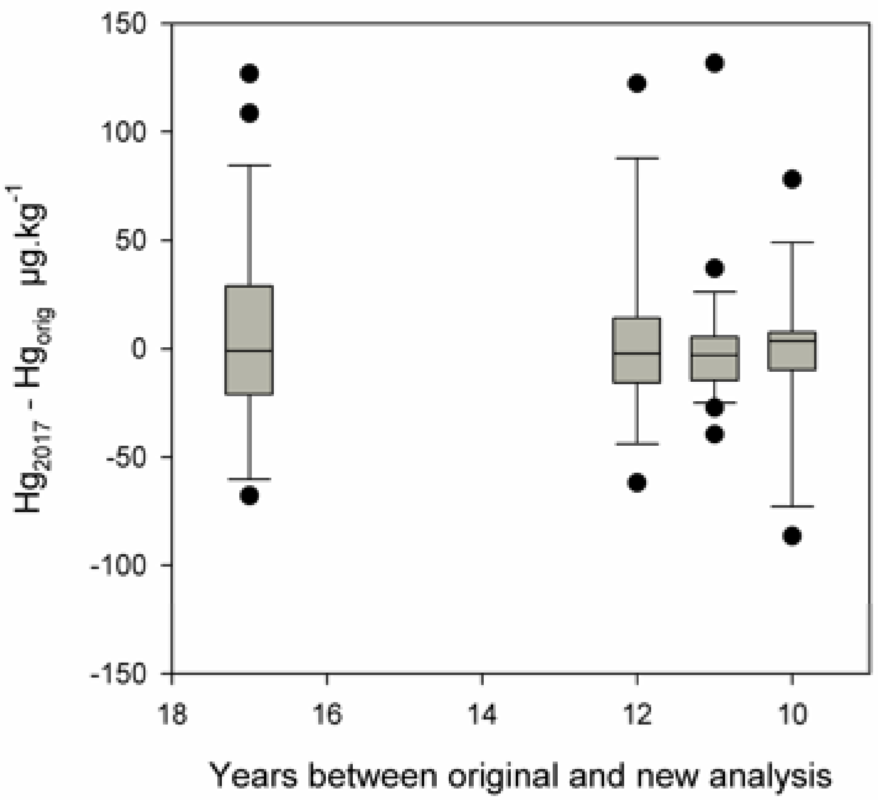
Initial and Archived Comparison



Wilcoxon Rank-Sum Test Differences

dataset	mean Hg_{orig} ($\mu g\ kg^{-1}$)	SD	mean Hg_{2017} ($\mu g\ kg^{-1}$)	SD	n	T	Z	p-value
all data	409	811	411	821	82	1651	0.233	0.815
separated based on site								
PL	204	145	205	134	29	214	0.076	0.940
PRI	1211	1602	1219	1629	16	67	0.052	0.959
TOK	253	91	251	92	10	17	1.070	0.285
LES	226	219	231	221	13	39	0.454	0.650
LYS	327	253	330	246	6	10	0.105	0.917
NPBS	107	190	100	159	8	9	1.260	0.208
separated based on year								
2000	204	145	205	134	29	214	0.076	0.940
2005	1211	1602	1219	1629	16	67	0.052	0.959
2006	238	173	239	174	23	108	0.912	0.362
2007	201	239	199	226	14	45	0.471	0.638
separated based on carbon content								
TC > 10%	759	1169	756	1189	34	253	0.761	0.447
TC < 10%	162	151	167	152	48	528	0.615	0.538
separated based on Hg concentration								
Hg < 85 ($\mu g\ kg^{-1}$)	47	21	48	26	19	93	0.080	0.936
Hg 85-201 ($\mu g\ kg^{-1}$)	148	38	151	40	21	96	0.678	0.498
Hg 201-399 ($\mu g\ kg^{-1}$)	284	52	270	64	20	85	0.747	0.455
Hg > 399 ($\mu g\ kg^{-1}$)	1094	1380	1095	1355	22	117	0.308	0.758

Effects of Archive Duration



More Results

- At one site (PL), 12 of 29 samples differed by >20% between original and new analyses – only site where original analyses performed in different laboratory, new measurement aliquots had to be prepared from sieved samples
- For all other sites – 4 of 53 samples differed by >20%
- ANCOVA to test for differences in the slopes and intercepts of linear regression relation between Hg concentrations for each sampling year and the Hg concentrations in 2017 – no significant differences in slopes or intercepts

Conclusions

- No significant differences in total Hg concentrations for the sites/samples examined here and collected in the Czech Republic
- No differences were apparent as function of storage duration, organic C content, or Hg concentration
- Greatest differences were apparent for samples that were analyzed in different labs and required re-alquoting
- More studies like this – need to systematically test different storage conditions and durations

Acknowledgements

- Study and paper originated with a suggestion by me to explore soil archiving for Hg – Tomas Navratil arranged for 2017 analyses
- Value of an opportunistic study
- Thank Tomas Navratil for including me in this study
- I assisted with some of the statistical analyses and helped write the text
- Paper in review at Chemosphere